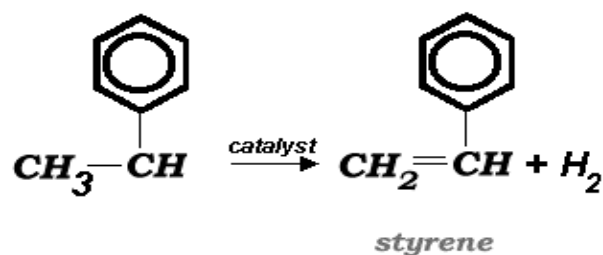


PROCESS DESCRIPTION

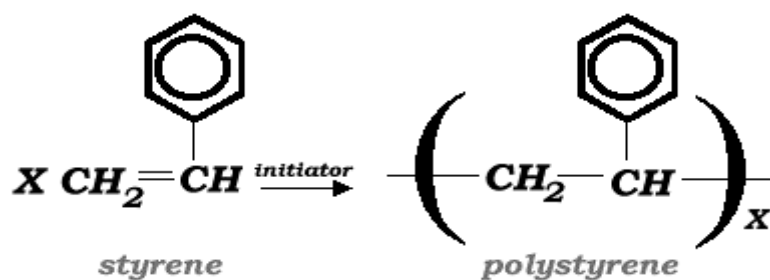
Manufacturing process:

Polystyrene is manufactured by the addition polymerization of styrene monomer unit. Dow Chemical is the world's largest producer with a total capacity of 1.8 million metric tones in the USA, Canada, and Europe (1996 figures). The main manufacturing route to styrene is the direct catalytic dehydrogenation of ethyl benzene:



The reaction shown above has a heat of reaction of -121 KJ/mol (endothermic). Nearly 65% of all styrene is used to produce polystyrene.

The overall reaction describing the styrene polymerization is:



This reaction is carried out in an inert organic solvent environment, which provides the reaction medium for this cationic polymerization reaction

The different methods available for styrene polymerization are:

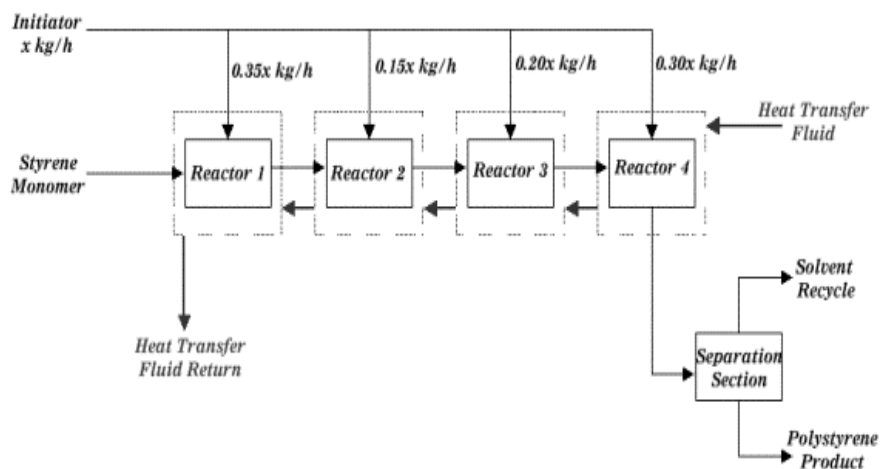
1. Solution (bulk) polymerization.
2. Emulsion polymerization.
3. Suspension polymerization.

Solution (bulk) polymerization:

Solution (bulk) polymerization is commonly referred to as mass polymerization in the industry. The vast majority of all polystyrene produced today is produced via this technology. The common solvents used in this process are the styrene monomer itself and ethyl benzene. The two types of mass polymerization are batch and continuous, of which continuous mass is by far the most popular.

Batch mass polymerization consists of a polymerization section containing agitated vessels polymerizing up to 80% conversion in a batch method. The polymerized solution is then pumped to a batch finishing section for either devolatilisation or plate and frame final polymerization and grinding.

The most widely used process for polymerization of polystyrene today is the continuous mass process. This solution is continuously prepared in a holding vessel and will then be injected into the reactor system.



Typical feed to the first reactor would consist of 50 weight percent styrene monomer, 100 ppm water (based on styrene weight), 2000 ppm boron trifluoride (based on styrene weight), with the balance being organic solvent. The polymerization reaction gives off heat that is carried away from the reactors by jacketing them with a heat transfer fluid. The temperature of the reactants should not vary by more than 15 °C throughout the reactor series. Temperature control is very important in this reaction because as the reaction temperature increases, the average molecular weight of the polystyrene decreases. The reaction temperature range is 40-70 °C. Temperature can also be controlled by intermediate shell and tube heat exchangers. Monomer conversions of up to 85wt% polystyrene are obtainable in these reactors.

Emulsion polymerization: Emulsion polymerization is generally used for polymerization of styrene with other monomers or polymers. It is not a generally commercially accepted method of producing crystal polystyrene or high impact polystyrene. Emulsion polymerization is carried out similarly to suspension polymerization except that the monomer droplets are microscopic in size.

Suspension polymerization:

This is also called pearl polymerization. It has proved highly efficient for large-scale production of polymers of high average molecular weight. By variation of the polymerization condition it is possible to produce a range of polymers with different properties and processing characteristics so that a number of grades are offered by the manufacturers to meet the differing requirements of the conversion process and the final product.

There are many different ways of making polystyrene using suspension process. Most producers use a batch process, although there is no technical reasons why a continuous process could not work. In the suspension process a number of small styrene drops 0.15-0.50mm in diameter are suspended in water. The reaction occurs within these

drops. To aid in the formation of proper size drops a suspending agent is used, and to keep them at that size a stabilizing agent is added. A catalyst is used to control the reaction rate.

Suspension polymerization offers considerable advantages over the single phase techniques in so far that heat removal control is no longer a problem but there are disadvantages such as the need to use a dispersing agent.

Detailed process of suspension polymerization:

Suspension polymerization is a batch system popular for speciality grades of polystyrene. It can be used to produce either crystal or high impact grades. In impact production, the styrene and rubber solution is bulk polymerized beyond phase inversion and is then suspended in water to create oil in water suspension utilizing soaps and suspending agents. The suspended droplets are then polymerized to completion, utilizing initiator and a staged heating profile. The water phase is used as a heat sink and heat transfer medium to a temperature-controlled jacket. For the production of crystal polystyrene the styrene monomer itself is suspended and polymerized via the same mechanism.

The requirements of polymerization are:

a] Initiator. b] Suspending agent. c] Stabilizing agent. d] Catalyst

Initiators: The initiators generally used are benzoyl peroxide and t-butylhydroperoxide.

Suspending agent: To aid in the formation of the proper size drops a suspending agent is added. Some typical suspending agents are methylcellulose, ethyl cellulose and polyacrylic acids. Their concentration in the suspension is between 0.01-0.5% of monomer charged.

Stabilizing agent: To keep the drops at proper size, a stabilizing agent is added. The

stabilizing agents are often insoluble inorganic such as calcium carbonate, calcium phosphates or bentonite clay. They are present in small amount than the suspending agents.

Catalyst: A catalyst is used to control the reaction rate. The catalysts are usually peroxides. The most common ones are benzoyl, diacetyl, lauroyl, caproyl and tert-butyl. Their concentration varies from 0.1-0.5% of the monomer charged. The ratio of monomer to dispersing medium is between 10 and 40%.
Polymerization temperature: Polymerization of styrene occurs at temperature range of 90-95⁰C.

Process description: The suspension method is carried out in large reactors equipped with agitators, the styrene monomer being maintained in the aqueous phase as droplets with a diameter varying between 0.4-1mm by use of a dispersing agent such as partially hydrolyzed polyvinyl acetate, inorganic phosphates or magnesium silicates. To reduce the cycle time of the reactors, the entering water and styrene will be preheated. The temperatures of the input streams will be set so as to obtain the desired reaction temperature. The water entering the reactor will be heated to 95⁰C. The bulk of the styrene is to be heated to 85⁰C before being charged. This is done in a vertical double pipe heat exchanger, which is directly above the reactor. To prevent the polymerization from occurring in the heat exchanger or piping system, there are to be no obstructions between this heat exchanger and the reactor. The catalyst, rubber stabilizer, and suspending agent are premixed in styrene and discharged by gravity into the reactor. This mixture will not be preheated, since it might polymerize. Typical water to monomer ratios is 1:1 to 3:1. A combination of two or more initiators is used with a programmed reaction temperature to reduce the polymerization time to a minimum for a given amount of residual styrene.

Purification steps and Extrusion: If the water can be removed using physical separation processes, then the styrene and the other impurities dissolved in it will also be discharged.

A centrifuge with a washing step will be used to do this. The material leaving the centrifuge has 1-5% water.

The final purification step is drying. The polystyrene leaving this unit must meet the specifications set. (0.03% water). Then it is passed through a devolatilisation extruder to remove the volatile residues and to convert the polymer into pellets.

It was assumed that 3% of polystyrene would be removed from the process in airveying, drying, centrifuging, transferring, or as bad as bad product. At least 95% of that which is lost in processing must be intercepted before it leaves the plant. Most of it can be removed and sold as off-grade material. This waste is split among the various streams leaving the processing area.